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Comparison of the degradation of *p*-hydroxybenzoic acid in aqueous solution by several oxidation processes

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Abstract

A comparative study is made of 12 methods of chemical oxidation applied to degrading *p*-hydroxybenzoic acid in aqueous solution. The oxidation processes tested were: UV, O_3, UV/TiO_2, O_3/Fe^{2+}, O_3/H_2O_2, O_3/UV, UV/H_2O_2, H_2O_2/Fe^{2+}, $H_2O_2/Fe^{2+}/O_3$, UV/H_2O_2/O_3, H_2O_2/Fe^{2+}/UV and O_3/UV/H_2O_2/Fe^{2+}. The 12 processes were ranked by reactivity. In a kinetic study, the overall kinetic rate constant was split up into three components: direct oxidation by UV irradiation (photolysis), direct oxidation by ozone (ozonation), and oxidation by free radicals (mainly $OH^{\cdot}$).

Keywords: *p*-Hydroxybenzoic acid; AOPs; Kinetics; Photolysis; Ozonation; Fenton's reagent

1. Introduction

Industries of olive oil extraction, table olive production, and alcohol distillation from different wine fractions give rise to highly contaminant wastewaters. This is a major environmental problem in Mediterranean countries in general, and particularly in certain areas of Spain and Portugal where there are a great many small plants.

Specifically, most of these wastewaters pollutant properties have been ascribed to phenolic compounds, because of their toxicity (Hamdi, 1992) and power to inhibit biological treatments (Borja et al., 1997). As a consequence of this situation and the more stringent regulations concerning effluents released into public rivers and streams, new technologies have been developed to reduce these refractory contaminants. Among them, chemical oxidations by UV radiation (Legrini et al., 1993; Yue, 1993) and ozone (Rice, 1981; Rice and Netzer, 1982) are increasingly used for the reduction of organic contaminants present in a variety of wastewaters from different industrial plants. However, this decomposition using single treatments may sometimes be difficult if the pollutants are present at low concentrations or if they are especially refractory to the oxidants. For such situations, it has been necessary to develop more effective processes for the destruction of the contaminants.

For example, systems based on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, have generated increasing interest due to their high oxidant power. These systems are commonly termed advanced oxidation processes (AOPs). The radicals are produced by combinations of ozone, hydrogen peroxide, UV radiation (Glaze et al., 1987; Glaze and Kang, 1989; Masten and Davies, 1994) and titanium dioxide (Ollis et al., 1989; Fox and Dulay, 1993; Pichat

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et al., 1993; Bahnemann et al., 1994), and also by the combination of hydrogen peroxide with ferrous ions in the so-called Fenton's reagent (Walling, 1975). These methods can provide almost total degradation as has been reported by several authors for the decomposition of a wide variety of organic contaminants (Peyton et al., 1982; Guittonneau et al., 1988; Legrini et al., 1993).

The phenolic compound *p*-hydroxybenzoic acid is very common in a great variety of agroindustrial wastewaters (olive oil and table olive industries, distilleries, etc.). It is found to be especially toxic and refractory to anaerobic biological treatment (Gonzalez et al., 1990). It was therefore chosen as a representative phenolic acid to comparatively study its degradation by several chemical methods.

The objectives were to provide data about the degree of removal, to report values of the kinetic rate constants for the global processes, and to compare the efficiency of the different advanced oxidation methods. Also, the increases obtained in the degradation levels due to the presence of free hydroxyl radicals in the combined oxidations compared to the single oxidation processes are determined, and the partial contributions of the $OH^{\cdot}$ radical pathway to the global oxidation process are calculated for the different AOPs studied.

2. Material and methods

Analytical grade *p*-hydroxybenzoic acid was obtained from Sigma, titanium dioxide (Degussa P-25) from Degussa Portugal and hydrogen peroxide (33% w/v) and ferrous sulfate heptahydrate from Merck.

The radiation source was a Heraeus TQ-150 medium pressure mercury vapour lamp which emits polychromatic radiation in the range from 185 to 436 nm. Ozone was produced from an oxygen stream in an ozone generator (Sander, mod. 301.7).

The reactor consisted of a 500 ml glass cylinder provided with the necessary elements (inlets for stirring, sampling, bubbling the gas feed in the ozonation experiments, venting and measuring the temperature) for the development of the different processes: photodecomposition, Fenton's reagent oxidation, ozonation and the different combinations of these oxidants. The radiation source was located axially, held in a quartz sleeve. An external water jacket surrounded the reactor in order to maintain a constant temperature.

All the experiments for the different oxidation processes were performed under the same experimental conditions of temperature 20°C and pH 5. In the experiments with hydrogen peroxide, the concentration was always 2.65×10^{-3} M. In the experiments with ozone, the gas flow rate used was 40 l/h and the ozone partial pressure at the input to the reactor was kept constant at 0.32 kPa. The emittivity of the UV lamp was 3.3×10^{-5} Eins/s (Benitez et al., 1997). The reaction volume was 350 ml in all cases, and the initial concentration of the compound was 100 ppm, equivalent to 7.24×10^{-4} M.

In the experiments with the presence of Fe^{2+}, the concentration of this ion was in all cases 10 times less than that of H_2O_2, which is the optimal ratio according to most authors (Tang and Huang, 1996). The titanium dioxide concentration in catalyzed experiments was 2 g/l.

The selected pH 5 was adjusted by adding orthophosphoric acid and sodium hydroxide. The *p*-hydroxybenzoic acid concentration in the samples withdrawn from the reactor at regular reaction times was determined by HPLC using a Waters Chromatograph equipped with a 996 Photodiode Array detector and a Nova-Pack C-18 column. Detection was at 254 nm with a mobile phase composed of a methanol: water:acetic acid mixture (10:88:2 in volume) at a flow rate of 1 ml/min.

The H_2O_2 concentration was determined by the colorimetric method proposed by Bader et al. (1988). In the ozonation experiments, gas ozone concentration was measured iodometrically by bubbling the gas stream through a potassium iodide solution (Rice et al., 1986).

3. Results and discussion

The first stage was to compare the 12 oxidation processes applied to the destruction of *p*-hydroxybenzoic acid. Fig. 1 shows the conversion curves versus reaction time for all the experiments carried out. Table 1 lists the semireaction times and the conversion attained at 5 and 10 min of reaction time.

As a first approximation, the oxidation processes were ranked from lesser to greater efficacy, according to the levels of conversion attained at 5 and 10 min of reaction time. The resulting efficacy ranking is as follows:

$$\begin{aligned} &UV < UV/TiO_2 < O_3 < O_3/Fe^{2+} = O_3/H_2O_2 \\ &\quad < O_3/UV < UV/H_2O_2 = O_3/H_2O_2/Fe^{2+} \\ &\quad < H_2O_2/Fe^{2+} < UV/H_2O_2/O_3 < H_2O_2/Fe^{2+}/UV \\ &\quad < O_3/UV/H_2O_2/Fe^{2+} \end{aligned}$$

In order to study further the improvements provided by the different AOPs, the different oxidation systems are divided into three groups, corresponding to the three basic oxidation processes from which they derive: UV irradiation, ozonation, and Fenton's reagent.

3.1. Oxidation processes deriving from the application of UV radiation

The overall reaction process is taken to consist of three contributions: direct oxidation by UV irradiation

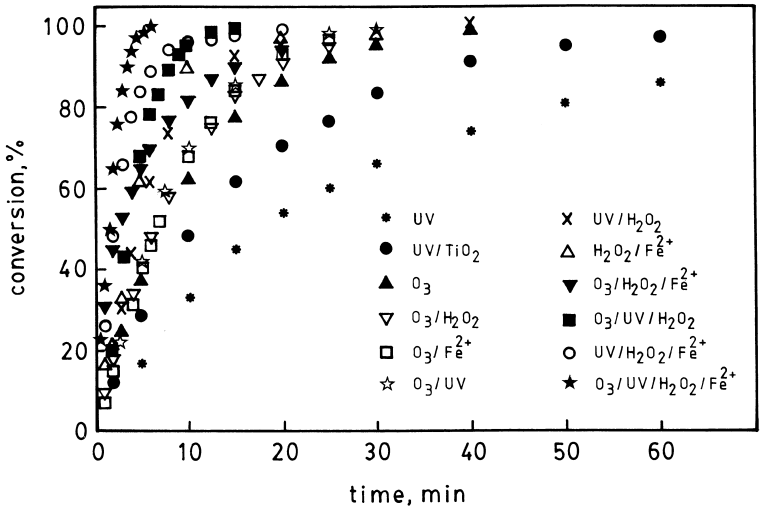

Fig. 1. *p*-Hydroxybenzoic acid conversion curves by different oxidant processes.

Table 1
Kinetic parameters of the different oxidation processes

Oxidation process	$t_{1/2}$ (min)	X_5 (%)	X_{10} (%)
UV	18.7	17	34
UV/TiO_2	10.1	29	49
O_3	8.02	37	62
O_3/Fe^{2+}	6.69	39	68
O_3/H_2O_2	6.16	41	68
O_3/UV	6.38	42	70
UV/H_2O_2	4.50	53	82
$O_3/H_2O_2/Fe^{2+}$	3.00	65	82
H_2O_2/Fe^{2+}	4.05	62	90
O_3/H_2O_2/UV	3.45	68	95
H_2O_2/Fe^{2+}/UV	2.09	84	96
O_3/UV/H_2O_2/Fe^{2+}	1.49	98	100

(photolysis), direct oxidation by ozone (ozonation), and oxidation by free radicals (mainly $OH^{\cdot}$):

$$P + h\nu \xrightarrow{k_P} P_{ox} \tag{1}$$

$$P + O_3 \xrightarrow{k_{O_3}} P_{ox} \tag{2}$$

$$P + OH^{\cdot} \xrightarrow{k_R} P_{ox} \tag{3}$$

With respect to direct oxidation of the compound by hydrogen peroxide, this was found experimentally not to exist. It also has to be noted that, at the reaction pH (pH = 5), ozone reacts with the compound directly (Eq. (2)) and not via free radicals (Sotelo et al., 1987).

It will also be assumed that the first two reactions (UV irradiation and ozonation) will take place whenever they form part of the combined oxidation system. This assumption is based on two facts: first, that in combined oxidation systems (binaries, ternaries, etc.) in which UV radiation is involved, only a minimal part of the emitted radiation is consumed in generating free radicals, most being absorbed by the compound; second, in combined systems involving ozone, the amount of ozone decomposed in generating free radicals is negligible with respect to the total amount of ozone.

In accord with this reaction scheme, the overall process rate can be written as the sum of three processes: direct photolysis (r_P), direct reaction with molecular ozone (r_{O_3}), and free radical reactions (r_R):

$$-r_T = [-dC_P/dt] = -(r_P + r_{O_3} + r_R) \tag{4}$$

$$= (k_P \cdot \Phi + k_{O_3} \cdot C_{O_3} + k_R \cdot [OH^{\cdot}]) \cdot C_P \tag{5}$$

$$(k_{P'} + k_{O_3'} + k_{R'}) \cdot C_P = k_T \cdot C_P \tag{6}$$

The order of efficacy in the oxidation systems deriving from UV irradiation was as follows:

$$UV < UV/TiO_2 < UV/O_3 < UV/H_2O_2 < UV/H_2O_2/O_3$$

Fig. 2 shows the disappearance curves of *p*-hydroxybenzoic acid in this group of experiments. Table 2 lists the values of the pseudo-first-order kinetic constants (k_T) obtained for each system. This constant was also split up into its three components: photolysis ($k_{P'}$), ozonation ($k_{O_3'}$), and free radical ($k_{R'}$).

It can be seen that there is a synergic effect when the different oxidation systems are combined, due specifically to the increase in the free radical component.

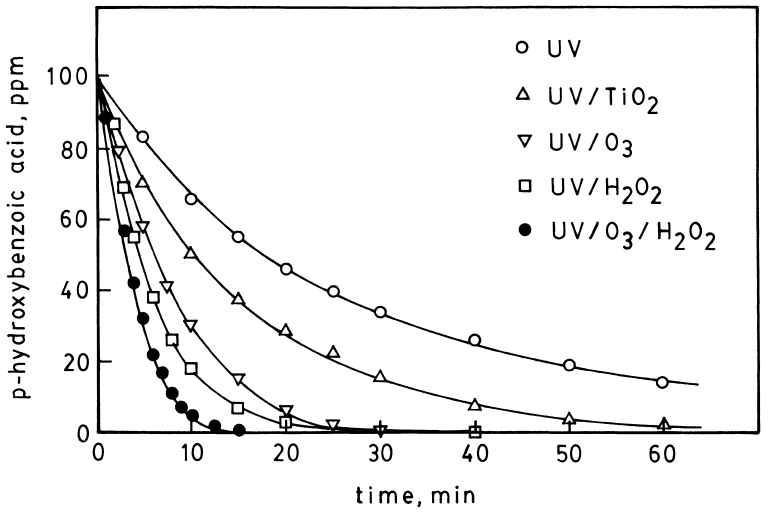

Fig. 2. *p*-Hydroxybenzoic degradation curves of oxidation processes deriving from the application of UV radiation.

Table 2
Split up of kinetic rate constants for processes deriving from the application of UV radiation

Oxidation process	k_T (min^{-1})	$k_{P'}$ (min^{-1})	$k_{O_3'}$[a] (min^{-1})	$k_{R'}$ (min^{-1})
UV	0.032	0.032	–	–
UV/TiO_2	0.063	0.032	–	0.031
UV/O_3	0.151	0.032	0.100	0.019
UV/H_2O_2	0.176	0.032	–	0.144
$UV/H_2O_2/O_3$	0.358	0.032	0.100	0.226

[a] See Table 3.

One observes in Table 2 that a binary UV/O_3 process is not the sum of two individual processes O_3 and UV. This is because of the generation, albeit at a very low concentration, of free radicals (Eq. (2)). This synergic effect can also be observed in the ternary process $UV/H_2O_2/O_3$, which is not equal to the sum of the binary UV/H_2O_2 process plus the simple process O_3. Neither is it equal to the sum of the three individual processes, so that there is a clear synergy involved. This synergy is the reason behind the recent trend towards using combinations of different oxidants.

One explanation of the improved results using the UV/H_2O_2 process with respect to the UV/O_3 system may be that in the production of an $OH^{\cdot}$ radical, the former process only requires 1/2 peroxide molecule and 1/2 photon, whereas the latter process requires 1.5 ozone molecules and 1/2 photon (Eqs. (7) and (8)). According to Eq. (5), the constant $k_{R'}$ depends on the concentration of $OH^{\cdot}$ free radicals generated.

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\cdot} \tag{7}$$

$$3O_3 \xrightarrow{h\nu} 2OH^{\cdot} \tag{8}$$

Also, while H_2O_2 is infinitely soluble in water and presents no problems related to mass transfer, ozone has a low solubility in water and presents the limitations in mass transfer that are typical of a solution of gases in liquids.

With respect to heterogeneous catalysis with TiO_2, photoexcitation with light of an energy greater than the TiO_2 band gap promotes an electron from the valence band to the conduction band, and leaves an electronic vacancy or hole (h^+) in the valence band. Thus the act of photoexcitation generates an electron–hole pair.

$$TiO_2 \xrightarrow{h\nu} TiO_2(h^+ + e^-) \tag{9}$$

In order to achieve chemically productive photocatalysis, electron-hole pair recombination must be suppressed. This can be achieved by "trapping" these species with the surface adsorbates. The photo-excited electrons are trapped by molecular oxygen:

$$e^- + O_2(\text{ads.}) \rightarrow O_2^-(\text{ads.}) \tag{10}$$

The principal hole traps are adsorbed water molecules and OH^- ions (Turchi and Ollis, 1990; Topalov et al., 1999) producing $OH^{\cdot}$ radicals.

$$h^+ + H_2O(ads.) \rightarrow OH^-(ads.) + H^+ \quad (11)$$

$$h^+ + OH^-(ads.) \rightarrow OH^{\cdot}(ads.) \quad (12)$$

Therefore, there coexist two parallel oxidation reactions in the UV/TiO_2 system: direct photolysis by UV irradiation, and free radical oxidation due to the hydroxyl radicals generated as in Eq. (12). The former route accounts for 51% of the total reaction, and the latter free radical route 49%.

3.2. Processes based on the application of ozone

Taking as reference the level of degradation attained at 5 and 10 min of reaction time, the different oxidation processes were ranked in terms of efficacy as follows:

$$O_3 < O_3/Fe^{2+} = O_3/H_2O_2 < O_3/UV < O_3/H_2O_2/Fe^{2+} < O_3/UV/H_2O_2 < O_3/UV/H_2O_2/Fe^{2+}$$

Fig. 3 shows the *p*-hydroxybenzoic acid degradation curves for this group of experiments. Table 3 lists the total pseudo-first-order kinetic constants and their three components for each of the oxidation processes.

Once it is found that the addition of Fe^{2+} or H_2O_2 by themselves exerts no oxidizing activity against *p*-hydroxybenzoic acid, it can be deduced that the addition of these substances has a slight synergic or catalytic effect on the oxidant activity of ozone, presumably due to free radical generation. Free-radical-mediated synergic effects were observed in the O_3/UV combination as well as in the above two combinations. It should be mentioned that in the system $O_3/H_2O_2/Fe^{2+}$, there exists neither synergy nor additivity of the two effects (Fenton's reagent + ozone). This may be because ozone interferes with the action of Fenton's reagent, probably by oxidizing Fe^{2+} to Fe^{3+}. This phenomenon is seen in Fig. 3: the combined Fenton's reagent+ozone system is faster to start with (when the Fe^{2+} concentration is high), but is eventually overtaken by Fenton's reagent.

With respect to the last two oxidation systems of Table 3, one observes more marked synergic effects together with greater importance of the free radical pathway in the oxidation process. One clearly sees that the

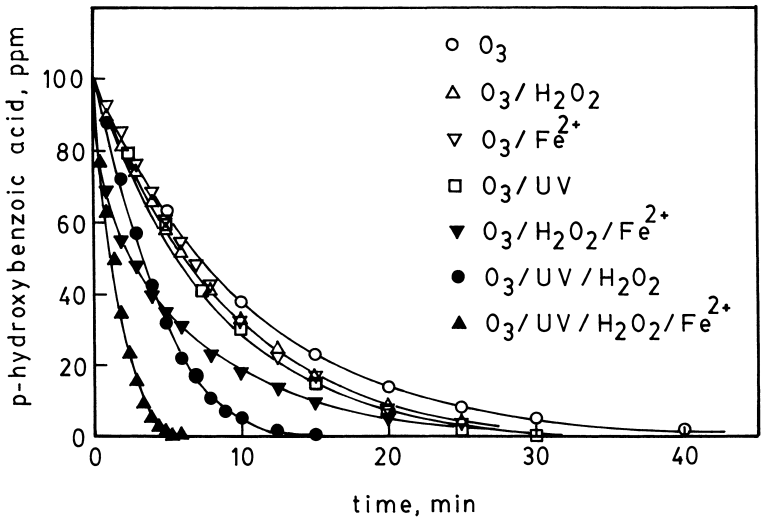

Fig. 3. *p*-Hydroxybenzoic degradation curves of processes based on the application of ozone.

Table 3
Split up of kinetic rate constants for processes based on the application of ozone

Oxidation process	k_T (min^{-1})	$k_{P'}$ (min^{-1})	$k_{O_3'}$ (min^{-1})	$k_{R'}$ (min^{-1})
O_3	0.100	–	0.100	–
O_3/Fe^{2+}	0.135	–	0.100	0.035
O_3/H_2O_2	0.122	–	0.100	0.022
O_3/UV	0.151	0.032	0.100	0.019
$O_3/H_2O_2/Fe^{2+}$	0.128	–	0.100	0.028
$O_3/UV/H_2O_2$	0.358	0.032	0.100	0.226
$O_3/UV/H_2O_2/Fe^{2+}$	0.869	0.032	0.100	0.737

$O_3/UV/H_2O_2$ system is not the simple sum of the systems UV/H_2O_2 and O_3, nor it is the sum of the three individual systems $UV + H_2O_2 + O_3$. The case is similar, although greater in degree, for the $O_3/UV/H_2O_2/Fe^{2+}$ system, which is far more effective than would be expected from the sum of the three oxidants (O_3 + UV +Fenton's reagent).

As can be seen from Table 3, the more oxidizing agents making up the oxidation system, the greater the synergic effect with the consequent increase in the free radical oxidation pathway.

The authors have also shown that the combination of hydrogen peroxide, UV radiation and ozone increased the fraction of absorbed ozone consumed, and deduced that the rate of total ozone mass transfer (in molecular or radical form) into the bulk liquid must be high under these conditions. This efficient ozone mass transfer, in combination with enhanced ozone consumption, implies, of course, greater economy in its use.

3.3. Oxidation systems based on Fenton's reagent

Considering the degree of conversion of *p*-hydroxybenzoic acid at 5 and 10 min reaction time, the order of reactivity of the oxidation systems is as follows:

$$Fe^{2+}/H_2O_2/O_3 < Fe^{2+}/H_2O_2 < Fe^{2+}/H_2O_2/UV < Fe^{2+}/H_2O_2/UV/O_3$$

Fig. 4 shows the disappearance curves for the experiments belonging to this group. Table 4 lists the pseudo-first-order rate constants and their three components.

As can be seen for the last two oxidation systems of Table 4, the synergic effect of the addition of ozone to the photo-Fenton's reagent system is very high, notable increasing the free radical pathway.

The synergic effect observed for the combined photo-Fenton's reagent system with respect to the sum of the two systems (Fenton's reagent + UV radiation) has recently been demonstrated. The UV/visible irradiation accelerates (H_2O_2/Fe^{2+}) reactions, improving the degradation rates of various organic pollutants, such as 4-chlorophenol (Ruppert and Bauer, 1993), PCB (Pignatello and Chapa, 1994) and herbicides (Sun and Pignatello, 1993). This enhancement has been explained as due to Fe^{3+}-photocatalyzed reactions, i.e., photolysis of hydroxide complexes of Fe^{3+} yielding hydroxyl radicals and regenerating Fe^{2+} (Eq. (14)) and photochemical reactions of complexes formed between Fe^{3+} and the organic substrate or its degradation intermediates

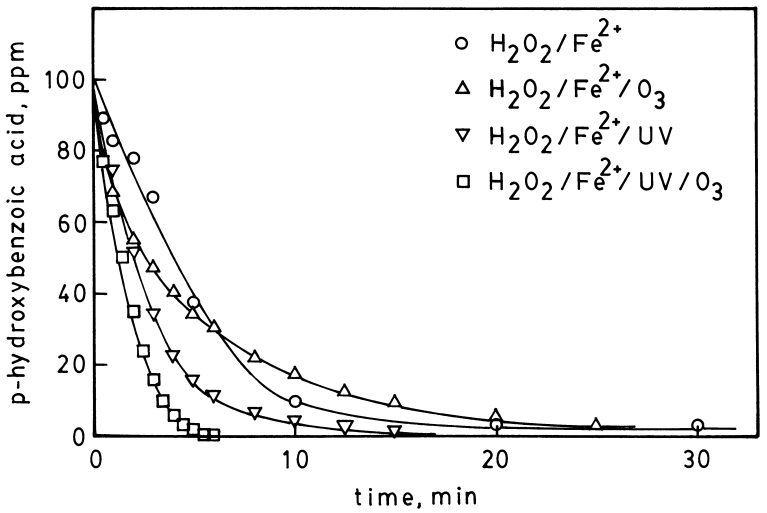

Fig. 4. *p*-Hydroxybenzoic degradation curves of oxidation systems based on Fenton's reagent.

Table 4
Split up of kinetic rate constants for processes based on Fenton's reagent

Oxidation process	k_T (min^{-1})	$k_{P'}$ (min^{-1})	$k_{O_3'}$ (min^{-1})	$k_{R'}$ (min^{-1})
$Fe^{2+}/H_2O_2/O_3$	0.128	–	0.100	0.028
Fe^{2+}/H_2O_2	0.227	–	–	0.227
$Fe^{2+}/H_2O_2/UV$	0.263	0.032	–	0.231
$Fe^{2+}/H_2O_2/UV/O_3$	0.869	0.032	0.100	0.737

(Eq. (15)), especially organic acids (Pignatello and Chapa, 1994):

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\cdot} \quad (13)$$

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH^{\cdot} \quad (14)$$

$$Fe(L)^{2+} \xrightarrow{h\nu} Fe^{2+} + L^{\cdot} \quad (15)$$

The Fenton's reagent and photo-Fenton's reagent systems perform better than the UV/H_2O_2 system because H_2O_2 has a low molar extinction coefficient in the UV region (e.g. $\varepsilon = 19.61\,l\,mol^{-1}\,cm^{-1}$ at 254 nm), rendering it susceptible to inner-filter effects from absorbing compounds in solution: *p*-hydroxybenzoic acid has the maximum absorbance wavelength of 254 nm. Also, H_2O_2 does not absorb at all above ~ 320 nm. A related method of producing $OH^{\cdot}$ from H_2O_2 is via Fenton's reagent (Eq. (13)). Fenton's reagent can be made catalytic by photoreducing the Fe^{3+} product in the near UV region (Eqs. (14) and (15)). The $Fe(OH)^{2+}$ ion absorbs light at wavelengths up to about 410 nm. Hence, the reaction can be carried out efficiently with longer wavelength light than other AOPs such as O_3/UV or H_2O_2/UV which require wavelengths below ~ 300 nm (Huston and Pignatello, 1999).

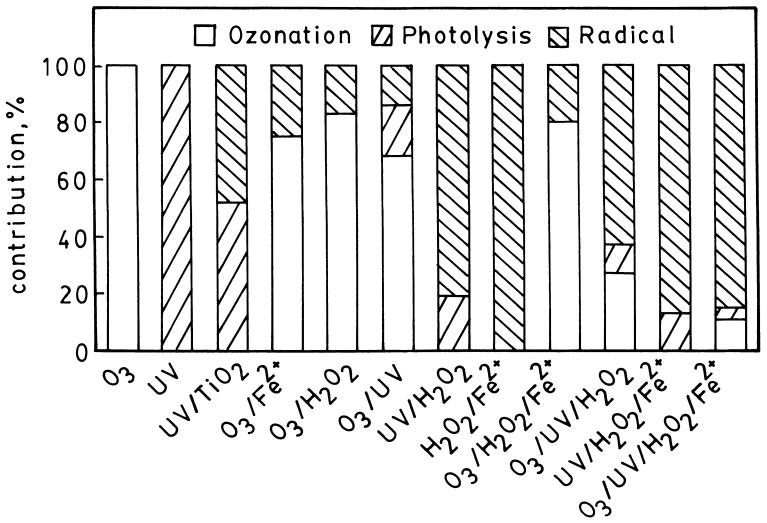

Fig. 5. Contribution of photolysis, ozonation and radicalary reaction in each oxidation process.

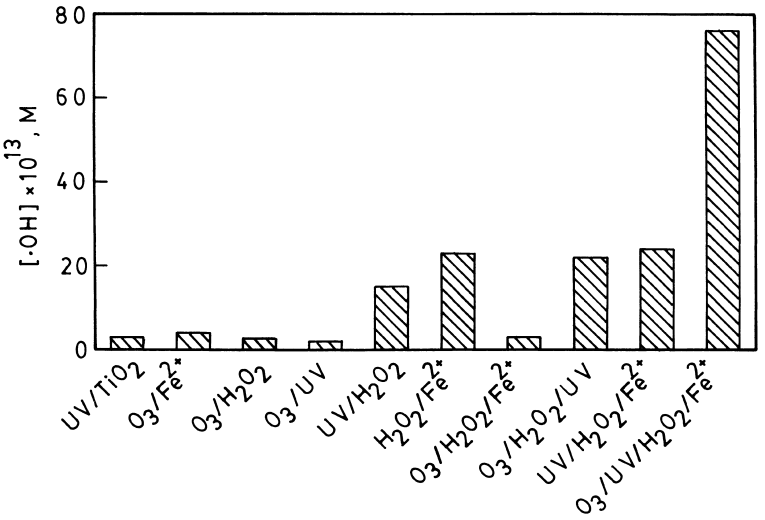

Fig. 6. Values of the hydroxyl radical concentration for each oxidation system.

Fig. 5 shows a summary of the importance of each of the three reaction routes (direct photolysis, ozonation, and free radicals) in each of the combined oxidation processes. One sees that the combined systems that have the greatest free radical component (> 80% of the overall oxidation process) are: Fe^{2+}/H_2O_2, $Fe^{2+}/H_2O_2/UV$, $O_3/UV/H_2O_2/Fe^{2+}$, UV/H_2O_2.

One may also calculate k_P and k_{O_3} from Eqs. (5) and (6), knowing the emittivity of the lamp $\Phi = 3.3 \times 10^{-5}$ Eins/s and the ozone concentration in the reactor $C_{O_3} = 2.97 \times 10^{-5}$ M, which was calculated from its corresponding Henry's constant (Sotelo et al., 1989). The resulting values for these two constants were 16.1 $Eins^{-1}$ for k_P and 56.1 l/(mol s) for k_{O_3}. For the free radical pathway, however, neither the value of k_R nor of $[OH^{\cdot}]$ are known. Therefore, the constant k_R was calculated by applying a comparative method (Gurol and Nekouinaini, 1984), using benzoic acid as reference compound since its reaction constant with the hydroxyl radical is well-described (Ashton et al., 1995). A value was thereby obtained for the reaction constant of the hydroxyl radical with *p*-hydroxybenzoic acid of 1.63×10^9 l/(mol s) at 20°C. Having determined this constant, the next step was to calculate the concentration of hydroxyl radicals for each of the oxidation systems employed. Fig. 6 shows the values of the hydroxyl radical concentrations for each oxidation system.

4. Conclusions

The order of reactivity deduced for the oxidation of *p*-hydroxybenzoic acid in aqueous solution was as follows:

$$\begin{aligned} UV < UV/TiO_2 < O_3 < O_3/Fe^{2+} = O_3/H_2O_2 \\ < O_3/UV < UV/H_2O_2 = Fe^{2+}/H_2O_2/O_3 \\ < Fe^{2+}/H_2O_2 < UV/H_2O_2/O_3 < Fe^{2+}H_2O_2/UV \\ < O_3/UV/H_2O_2/Fe^{2+} \end{aligned}$$

There were also seen to exist clearly synergic effects when two or more simple oxidation systems were combined. This synergy was reflected in a marked increase in the free radical reaction pathway. The effect was also observed to increase with the complexity of the oxidation system used. The only exception arose in comparing the Fenton's reagent system with the combined Fenton's reagent–ozone system, in which case there seems to be interference of the oxidant action of ozone with Fenton's reagent. This combination is not, therefore, advisable in the present case.

In light of the present results, it may be stated that combined oxidation processes, consisting of different individual oxidant systems, seem to represent a clear alternative to the usual simple oxidation systems.

Acknowledgements

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